

# Analysis by Redox Titration

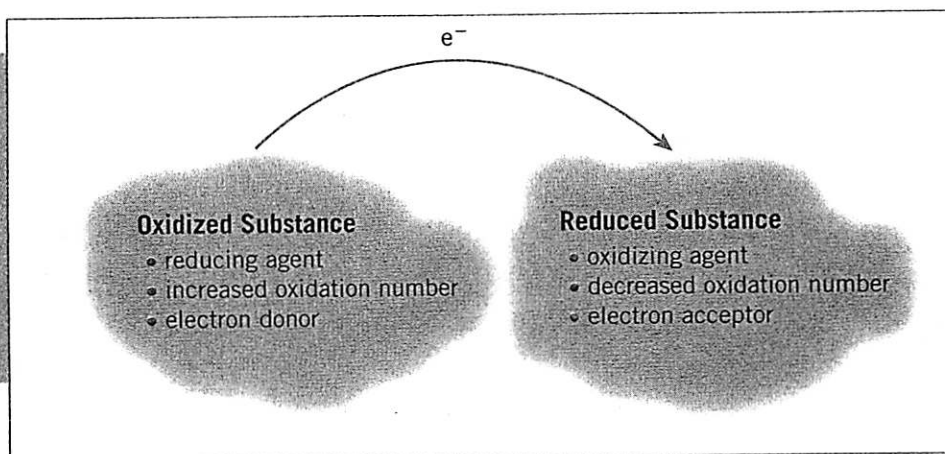
## PURPOSE

- Standardize a  $\text{KMnO}_4$  solution using iron(II) ("ferrous") ammonium sulfate as a standard
- Determine the concentration (mass percent and molarity) of a preparation of  $\text{H}_2\text{O}_2$
- Calculate the mass percent of iron in a consumer iron supplement

## INTRODUCTION

One common reaction type in chemistry is **oxidation-reduction**. It involves the transfer of electrons from one species to another. A species undergoes **oxidation** when a loss of electrons occurs. A substance undergoes **reduction** when it gains electrons. This process always occurs in pairs because it is a transfer from one species to another. A reducing agent is a species that causes reduction by donating electrons to another species, causing its oxidation number to decrease. Therefore, a reducing agent is itself always oxidized and its oxidation number is always increased. An oxidizing agent causes oxidation in another species by accepting that species' electrons, allowing oxidation (and increase of oxidation number) of the other species. Therefore, an oxidizing agent is itself always reduced and its oxidation number decreases.

**Figure 9.1**  
Whereas in acid-base reactions protons are transferred from one substance to another, in redox reactions electrons are transferred.



There are two general types of oxidation-reduction, or **redox**, equations. One signal of a redox reaction is the presence of an elemental form as a reactant. Other redox reactions occur in solution and may involve ionic forms. Frequently they involve common oxidizing agents such as the permanganate, chromate, or dichromate ions. In each of these, the metal cation has increased its oxidation number to or near its maximum. For example, manganese has lost seven electrons (the  $4s^2$  and  $3d^5$  electrons) to attain +7. Therefore, the manganese can only be reduced, gaining electrons from and causing oxidation of another species. These reactions are usually specified as being in acidic or basic (alkaline) solution.

The **balancing** of a redox equation is not done by conservation of mass or by counting numbers of atoms. Rather, the redox reaction is described by balancing the loss of electrons from one species and the gain of electrons from another. Because there is only one transfer of electrons in the reaction, the loss and gain of electrons must match. To facilitate the bookkeeping of electron transfers, **oxidation numbers (ON)** are assigned to each atom represented in each species; the oxidation number should not be thought of as the same as the actual charge in the compound or ion. Rules for assigning oxidation numbers can be summarized as follows:

- Atoms in elemental form have zero as an oxidation number. Thus, atoms in Fe, F<sub>2</sub>, P<sub>4</sub>, or S<sub>8</sub> all have an ON of 0.
- Monoatomic ions have an oxidation number equal to the charge on the ion. Hence, the ON of chloride is -1 while that of sulfide is -2.
- When combined with other atoms, atoms of group 1A (alkali metals) always have an ON of +1; atoms of group 2A (alkaline earth metals) always have an ON of +2.
- Combined oxygen always has an ON of -2 (except for peroxide or when combined with fluorine).
- Combined hydrogen always has an ON of +1 (except for hydrides).
- Combined fluorine always has an ON of -1.

The ON of any other atom must be determined from its context. The sum of all ON within a compound must be zero (thus the ON of sulfur in H<sub>2</sub>SO<sub>4</sub> must be +6). Within a polyatomic ion, the sum of ON must equal the overall charge on the ion (thus the ON of phosphorus in PO<sub>4</sub><sup>3-</sup> must be +5 because  $(-3) = 4(-2) + (\text{ON of P})$ ).

**Troubleshooting** To complete this and many other labs properly, it is crucially important to learn the definitions of oxidation-reduction chemistry carefully and thoroughly. Because the process is a directional transfer of electrons, getting one definition backward will cause all other processes to be reversed, and chaos will ensue!

Here is a technique for balancing redox equations that rarely fails:

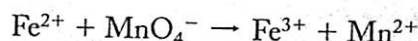
1. Separate the equation into two half-reactions. One must contain an oxidation, and the other must include a reduction.
2. Balance each half-reaction separately.
  - a. Balance the element oxidized or reduced.
  - b. Balance any elements other than oxygen or hydrogen.
  - c. Balance oxygen by adding water in the form of H<sub>2</sub>O.
  - d. In *acidic* solution, balance hydrogen by adding protons (H<sup>+</sup>). In *basic* solution, balance hydrogen by adding water in the form H-OH, and then immediately add the same number of hydroxides (OH<sup>-</sup>) to the other side of the equation.
  - e. Balance the total charge on each side of the equation by adding electrons (e<sup>-</sup>) to the side that is more positive.
3. Equalize the number of electrons lost and gained in the separate half-reactions by multiplying each by an integer. (You will remember this technique from math class as being similar to determining the LCM, or least common multiple.) For example, if the oxidation loses 2 electrons while the reduction gains 3 electrons, the least common multiple would be 6. Thus, you should multiply the oxidation by 3 and the reduction by 2 to acknowledge a transfer of 6 electrons.
4. Add the two half-reactions together. The electrons should cancel out from each side of the equation. You should be able to cancel other species as well. Protons, hydroxides, and waters frequently will cancel. Remember that H<sub>2</sub>O and H-OH both mean water; they are written differently to balance oxygen and hydrogen, respectively.

5. Check to be sure that there is the same total charge on each side (though the total may be zero, it is not required to be zero—just the same). Then, check the total number of oxygen atoms on each side. If both the total charge and the number of oxygens balance, it is highly likely that you have balanced the overall reaction correctly.

**Procedure Preview** In this lab, iron(II) ammonium sulfate hexahydrate (“FAS,” or “ferrous ammonium sulfate”) will be titrated with a potassium permanganate solution to standardize it. Then a hydrogen peroxide/sulfuric acid solution will be titrated with the standardized  $\text{KMnO}_4$  solution to analyze the hydrogen peroxide found in a commonly available consumer product. Finally, a solution of the iron supplement will be titrated with  $\text{KMnO}_4$  solution to quantify the actual iron in the supplement and to compare it to the manufacturer’s claim.

### Pre-Lab Questions

1. What is meant by “standardization”?
2. Balance in *acid* solution:



3. “FAS” is a nickname for iron(II) ammonium sulfate hexahydrate. Why is it used as a standard in this experiment?
4. Balance this redox reaction: potassium permanganate, hydrogen peroxide, and sulfuric acid react to form manganese(II) sulfate, potassium sulfate, oxygen gas, and water.
5. In your lab notebook, draw data tables that list the measurements required for this lab. The tables will be filled in as the experiment is performed.

### MATERIALS

- ~0.01 M  $\text{KMnO}_4$
- 3%  $\text{H}_2\text{O}_2$
- 6 M  $\text{H}_2\text{SO}_4$
- “FAS”
- mortar and pestle
- micro-burets (see Appendix B)
- micro-stir bars (see Appendix C)
- 250-mL Erlenmeyer flask
- 50-mL buret (see Appendix A)
- 25-mL volumetric flask

### PROCEDURE

#### I. Standardization of Potassium Permanganate Solution

- Step A** Measure out 0.2000 g FAS (your sample need not be exactly that amount, but you do need to know exactly how much you have).
- Step B** Dissolve the FAS sample in approximately 25 mL distilled water. If the sample does not dissolve readily, heat and stir the solution.
- Step C** Prepare a 50-mL buret for use with the  $\text{KMnO}_4$  solution (refer to Appendix A, “Care and Feeding of the Buret”). After cleaning, be sure to rinse the buret with  $\text{KMnO}_4$  solution. Fill the buret with  $\text{KMnO}_4$  solution and run some through the tip of the buret. Note initial volume of the permanganate solution in the buret.
- Step D** Add 1 mL 6 M  $\text{H}_2\text{SO}_4$  to the FAS solution.
- Step E** Titrate the FAS solution with  $\text{KMnO}_4$  solution until a faint purple color persists for at least thirty seconds. Be sure to swirl or stir the solution continuously. Note the final volume of  $\text{KMnO}_4$  solution in the buret.
- Step F** Repeat.

### Calculations

1. Calculate the number of moles of FAS.
2. Calculate the number of moles of  $\text{Fe}^{2+}$ .
3. Calculate the number of moles of  $\text{MnO}_4^-$ .
4. Calculate the molarity of  $\text{MnO}_4^-$ .

### Post-Lab Questions

1. Does FAS require special safety concerns? Obtain a Material Safety Data Sheet (MSDS) to verify.
2. Is potassium permanganate a safety problem? Obtain an MSDS to verify.

### PROCEDURE (continued)

#### II. Analysis of Hydrogen Peroxide by Redox Titration

- Step A** Refer to the previous standardization of the potassium permanganate solution.
- Step B** Using a micro-buret, measure 1.250 mL  $\text{H}_2\text{O}_2$  solution into a 50-mL Erlenmeyer flask.
- Step C** Add 1 mL of 6 M  $\text{H}_2\text{SO}_4$ .
- Step D** Drop a micro-stir bar into the solution, set the flask onto a stirring/hot plate, and establish a gentle stirring rate. Add some distilled water if necessary to allow smooth mixing. Do not heat the solution.
- Step E** Using the same  $\text{KMnO}_4$  buret as in the standardization analysis, titrate the hydrogen peroxide/sulfuric acid solution with  $\text{KMnO}_4$  solution until a pale persistent purple exists. The characteristic color of the permanganate should last at least 30 seconds before fading.
- Step F** Repeat. If the result of the second trial is not within 5% of the first, repeat until a coherent result is reached.
- Step G** Mass a clean, dry 25-mL volumetric flask. Fill to the etched line with  $\text{H}_2\text{O}_2$  solution and mass again.

### Calculations

1. Calculate the density of the  $\text{H}_2\text{O}_2$  solution.
2. Calculate the number of moles of  $\text{KMnO}_4$  used in the titration.
3. Calculate the number of moles of  $\text{H}_2\text{O}_2$  in the original sample.
4. Calculate the mass of  $\text{H}_2\text{O}_2$  in the original sample.
5. Calculate the mass percent of  $\text{H}_2\text{O}_2$  in the original sample.
6. Calculate the molarity of  $\text{H}_2\text{O}_2$  in the original sample.

### Post-Lab Questions

1. How does the calculated mass percent of hydrogen peroxide compare to the advertised mass percent?
2. What is the percent error?
3. Why is it that the calculated and advertised figures might be different?
4. What are the measurement errors in this experiment and how significant are they?

**Post-Lab  
Questions**  
(continued)

5. What other reasons might exist to explain any discrepancy between the experimental and advertised values?
6. How is hydrogen peroxide used by consumers and in industry? Are there safety concerns? Obtain a Material Safety Data Sheet (MSDS) to verify any concerns.

**PROCEDURE**  
(continued)

**III. Analysis of Iron Supplement by Redox Titration**

**Step A** Mass the tablet or capsule of the iron supplement.

**Step B** If you have a tablet, crush it carefully with mortar and pestle. Put the crushed tablet in about 25 mL distilled water. Rinse mortar and pestle with distilled water to capture any residue. If it does not dissolve readily, heat and stir the solution. If using a gel capsule, carefully open the capsule and pour the contents into about 25 mL distilled water. Rinse any residue from the inside of the capsule. Heat and stir if necessary.

**Step C** Acidify the solution with 1 mL 6 M  $\text{H}_2\text{SO}_4$ .

**Step D** Titrate with  $\text{KMnO}_4$  solution to a pale persistent purple. Be sure to note the initial and final volume from the buret.

**Step E** Repeat.

**Calculations**

1. Calculate the volume of  $\text{KMnO}_4$  required.
2. Calculate the number of moles of  $\text{MnO}_4^-$  required.
3. Calculate the number of moles of  $\text{Fe}^{2+}$  required.
4. Calculate the number of grams of  $\text{Fe}^{2+}$ .
5. Calculate the mass percent of iron in the tablet or caplet.

**Post-Lab  
Questions**

1. Does the mass of iron that you calculated agree with the manufacturer's information as stated on the packaging? What is the percent error?
2. Suppose that the tablet contained a small quantity of another metal that could be oxidized by the permanganate solution. How would this affect the mass of iron that you calculate?
3. Suppose that the tablet included a nonreactive green coating. How might this affect the results of your titration?
4. Why did you add sulfuric acid before titrating?